The University of Chicago

Intermediate and Complex Ions. V. The Solubility Product and Activity of The Ions in Bi-Bivalent Salt

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL OF SCIENCE IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTY

BY

H. M. PAINE

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[Reprinted from a paper by William D. Harkins and H. M. Paine.]

INTERMEDIATE AND COMPLEX IONS. V. THE SOLUBILITY PRODUCT AND ACTIVITY OF THE IONS IN BI-BIVALENT SALTS.[1]

The first evidence which indicates that *all salts* which give, on complete ionization, 3 or more ions, ionize in steps in such a way as to give intermediate ions, was presented by Harkins[2] in 1911. The earlier idea was that intermediate ions are present in aqueous solution of some of the salts of higher types, but not in all cases. Thus Abegg and Spencer,[3] in 1905, considered that thallous oxalate gives rise to an intermediate ion, but potassium oxalate does not, while in 1911 Jellinek[4] concluded that intermediate ions are present in solutions of sodium sulfate, but not when potassium sulfate is the solute. Such salts are mercuric chloride, cadmium chloride, and lead chloride were commonly believed to give intermediate ions, but the more ordinary salts were in general supposed to ionize in one step or else to give only a negligible fraction of intermediate ions. Perhaps the strongest evidence in favor of ionization in one step

[1] This series of papers was begun by W. D. Harkins in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology and has been continued in the laboratory of the University of Chicago with the consent of Professor A. A. Noyes.

[2] *J. Am. Chem. Soc.*, **33**, 1836–72(1911); Harkins and Pearce, *Ibid.*, **37**, 2679(1916).

[3] *Z. anorg. Chem.*, **46**, 406 (1905).

[4] *Ibid.*, **76**, 309 (1911).

was found in the fact that in solutions of uni-bivalent salts the transference number is independent of the concentration. The work of Harkins indicates, however, that the percentage of intermediate ion is not negligible, but for salts of the type of potassium sulfate is 18% for 0.01 *N* solutions, 35% at 0.1 *N*, and rises to 46% in a normal solution, these being the percentages for the KSO_4^- ion.

In a study of the solubility of uni-bivalent salts it was found that whereas the addition of a salt with a common univalent ion decreases the solubility of the uni-bivalent salt very greatly, just as would be expected, the addition of a salt with a common bivalent ion has an entirely different effect from what had previously been supposed. In other words, the solubility curve in the latter case, at least where the saturating salt has a solubility of 0.05 *N* or more, has another form than that which would be predicted from the solubility product principle upon the basis of the usual assumptions. Instead of falling rapidly as the concentration of the added salt increases, the solubility of the saturating salt decreases[1] at first slightly but then increases.

When salts of the bi-bivalent type are used as saturating salts it is impossible to add a salt with a common univalent ion; but when salts with *bivalent* common ions are added to solutions of calcium sulfate (see Fig. 1), the solubility curves have somewhat the same form as when the saturating salt is of the uni-bivalent type. The explanation given by Harkins for the peculiar solubility curve of the uni-bivalent salts, was that it is due to the presence in such solutions of a considerable percentage of intermediate ions such as KSO_4^-, $BaCl^+$, etc.

It was found that the presence of intermediate ions in solution could also be easily recognized from the slope of the curve representing the solubility of the un-ionized part of the saturating salt when the concentration of the un-ionized part is calculated on the basis of the usual assumptions, which are as follows: (1) That the isohydric principle is valid, (2) that the usual method of calculating percentages ionization is correct, and (3) that no intermediate ions are present in the solution. Now, it happens that the deductions obtained by this method of detecting intermediate ions hold in all probability even if (1), the isohydric principle is not valid, and (2) if the usual method of calculating the percentage ionization is incorrect. This is true because no use is made of the absolute values of the solubility of the un-ionized part of the salt as calculated, and the only essential feature of the method is a proper comparison of the slopes of the calculated solubility curves for the non-ionized parts of uni-univalent and uni-bivalent salts. Thus, when calculated in the usual

[1] In the case of highly soluble salts of this type this initial decrease is absent, and the curves have the form which would be expected if the added salt had no ion in common with the saturating salt.

way, such curves for the *uni-univalent* salts slope rapidly downward as the total ion concentration (or the concentration of the added salt) increases. Now, if similar curves are constructed for *uni-bivalent* salts, it might be expected that they would have a somewhat similar form, and this is exactly what is found when the added salts used are such as would have little effect upon the calculated solubility of the un-ionized part when intermediate ions are present. The only salts of this kind are those with *no common ion.* In this case the curves for uni-univalent and uni-bivalent salts lie almost exactly parallel (compare with Fig. 3). However, when the added salt contains a common bivalent ion, the curves, when calculated on the basis of the third assumption, *i. e.*, that no intermediate ions are present, should not show the same slope if intermediate ions are present in considerable quantity. From the change in the slope of the curve it would be possible to form some idea of the amount of the intermediate ion present, although a quantitative estimate can be made much more accurately by the use of other methods. Now, if intermediate ions are present in the saturating salt, the calculated solubility of the un-ionized part should decrease much more rapidly when the added salt contains a common univalent ion, and, on the other hand, when a salt containing a common bivalent ion is added, this solubility should either decrease *less* rapidly or if the relative number of intermediate ions is large, the calculated solubility curve should rise instead of falling, and this latter has been found to be the case for uni-bivalent salts. It will be seen that this method of showing the presence of intermediate ions, and also something of their relative amount, depends upon the deviation of the calculated solubility curves from the normal slope, since at least the greater part of the deviation is caused by the false assumption that intermediate ions are absent.

When it is realized that more than half of the salts commonly used are higher type salts, it will be seen that it is important to extend this investigation to a study of types still higher than the uni-bivalent type already studied.[1] The next most important type of salts is the bi-bivalent; and in this type of salts there is a reversion from the tri-ionic salts previously investigated to di-ionic salts, which, with respect to the number of ions formed by a simple ionization, would seem to belong to the same type as the di-ionic uni-univalent salts. Since, by their simple ionization the bi-bivalent salts would give the same number of ions per molecule it might be expected that the curve for the solubility of the un-ionized part should be of the same general form as for the uni-univalent salts, provided that the ionization of the bi-bivalent salts is entirely a simple one.

[1] Harkins and Pearce, *J. Am. Chem. Soc.*, 37, 2679 (1916) have shown that uni-trivalent salts give a large number of intermediate ions in solution.

In view of these interesting ionization relations of trionic and still higher type salts, a study of sparingly soluble bivalent salts was undertaken with calcium sulfate as a type salt of this group. Its solubility and conductance were determined in pure water and also in solutions of various concentrations of copper sulfate, magnesium sulfate, and potassium nitrate. Density determinations were made on all mixtures and all weighings were corrected to vacuum. In the calculations the atomic weights for 1910 were used.

Preparation of Salts and Solutions.

The water used for this investigation had in no case a greater specific conductance than 0.7×10^{-6} and the average value in the bottles in which it was stored was 0.6×10^{-6}.

Calcium Sulfate.—This salt was made by the addition of a very dilute potassium sulfate solution to to very dilute calcium chloride solution. Kahlbaum's "Zur Analyse" salts were used and the work carried out in special vessels of resistance glass. The calcium sulfate was washed thoroughly and rotated with several successive portions until the conductivity became constant. This salt was preserved in glass-stoppered resistance glass bottles.

Gypsum.—For comparison some very clear plates of gypsum were obtained from Dr. A. D. Brokaw of the Geology Department.

Magnesium Sulfate.—Kahlbaum's "Zur Analyse" salt was twice recrystallized from conductivity water and a stock solution made up and analyzed by evaporation in platinum and weighing as magnesium sulfate.

Copper Sulfate.—Kahlbaum's "Zur Analyse" salt was twice recrystallized from conductivity water.

Potassium Nitrate.—Baker's potassium nitrate was recrystallized twice from conductivity water.

Methods of Analysis.

Calcium.—Calcium was determined by careful precipitation with ammonium oxalate from hot solution; after standing 4–6 hours, the calcium oxalate was filtered, washed with water containing a little ammonium oxalate, ignited in tared platinum crucibles and weighed as calcium oxide. Where copper was present it was removed from a very dilute solution by precipitation with hydrogen sulfide. The separation of magnesium from calcium presented difficulties because of the well-known fact that the quantitative separation of small amounts of calcium from much larger amounts of magnesium is unsatisfactory. The method proposed by Cameron and Bell[1] leaves much to be desired from the standpoint of accuracy. A plate of pure gypsum rotated in 25 cc. of conductivity water showed a loss equivalent to solubility of 2.067 g. per 1000 g. solution. The solution from this gave 2.083 g. $CaSO_4$ per 1000 g. of solution by the oxalate method, while the specific conductance was 0.0022115 ohms, almost the same as that for the prepared salt (0.0022148). This method was used therefore only in solutions of comparatively high concentration of magnesium sulfate. For the more dilute solutions the method proposed by Richards, McCaffery and Bisbee[2] was used.

Experimental Methods.

An excess of the calcium sulfate was rotated with water or solution of a salt in a 500 cc. glass stoppered resistance glass bottle which had been "steamed out" and

[1] *J. Phys. Chem.*, 10, 212 (1906).

[2] *Proc. Am. Acad.*, 36, 375 (1901).

thoroughly seasoned. The temperature was measured by a thermometer which had been compared with a certified Baudin thermometer. For each determination saturation was approached both from under-saturation and supersaturation. The solutions were filtered in the thermostat and the first 50 cc. rejected, in order to prevent errors due to adsorption. In the experiments with copper sulfate the concentration of copper was determined for each bottle separately. In the other series solutions were carefully made up in calibrated flasks from a weighed amount of standard solution. The calcium sulfate was finally carefully washed on a platinum cone with a large amount of the solution, and quickly transferred to the bottle, which was then filled up with solution and rotated as usual.

The conductivity measurements were made in the usual way with a roller bridge carefully standardized. The apparatus was similar to that used by Washburn.[1] Great care was taken throughout the work to exclude carbon dioxide from the solutions. The bottles were all filled with carbon dioxide-free air and all solutions and water carefully protected from contact with the air by soda lime trains.

Experimental Data.

The results of the solubility determinations of calcium sulfate in solutions of copper sulfate are given below in Table I, in Potassium nitrate in Table II*a*, in magnesium sulfate in Table II*b*, and those for gypsum in magnesium sulfate in Table II*c*.

The solubility of calcium sulfate in solutions of copper sulfate, magnesium sulfate, and potassium nitrate, together with the conductances of all of the solutions of the pure salts and of the mixtures, were determined by us, because none of the previous work on calcium sulfate gave extensive enough conductivity data for our purpose. The solubility data are plotted as undotted lines in Fig. 1, while the dotted lines represent the work of Cameron with potassium and sodium sulfates as the added salts. Other data of a similar nature may be found in papers by Sullivan[2] and by Cameron[3] and his associates.

The curves in this figure, which represent the addition of the common bivalent ions, do not have the form to be expected when a common ion is added, in fact, as is shown most clearly in Fig. 1, at a very low concentration (0.15 *N*) the copper sulfate curve changes to the form to be expected when a salt with no common ion is added, while that for magnesium sulfate changes at about 0.35 *N*. The form of these curves is somewhat the same as that previously found when a salt with a common bivalent ion is added to a solution in which the saturating salt is unibivalent and has a solubility of 0.07 *N* or more. The principal difference is that the initial solubility drop is greater in the case of the bi-bivalent salts. This change in the form of the curves representing the common ion effect has

[1] *J. Am. Chem. Soc.*, **35**, 177 (1913).

[2] *Ibid.*, **27**, 532 (1905).

[3] Cameron and Seidell, *J. Phys. Chem.*, **5**, 643–55 (1901); Cameron, *Ibid.*, **5**, 56 (1901); Seidell and Smith, *Ibid.*, **8**, 493 (1904); Cameron and Bell, *J. Am. Chem. Soc.*, **28**, 1220 (1906); Cameron and Bell, *J. Phys. Chem.*, **10**, 212 (1906); Cameron and Brezeale, *Ibid.*, **8**, 337–40 (1904).

TABLE I.—SOLUBILITY OF CALCIUM SULFATE IN SOLUTIONS OF COPPER SULFATE.

Copper sulfate.				Calcium sulfate.					
Per liter of solution. G.	Per 1000 g. solution G.	Equivalents per liter of solution.	Per 1000 g. water. G.	Per 1000 g. solution. G.	Per liter solution. G.	Equivalent concentration per liter.	Per 1000 g. water. G.	Specific conductance of mixture.	d_4^{25} of mixture.
0.0	0.0	0.0	0.0	2.0854	2.0835	0.03064	2.0897	0.0022148	0.99911
1.9963	1.996	0.025010	2.002	1.8435	1.8458	0.027113	1.8511	0.0031580	1.0010
7.9758	7.922	0.099925	7.998	1.671	1.6823	0.024711	1.687	0.0061348	1.0069
16.082	15.842	0.20147	16.128	1.661	1.6860	0.024767	1.691	0.009680	1.0149
33.810	32.67	0.42358	33.838	1.7468	1.8037	0.026493	1.8093	0.016383	1.0324
155.01	134.65	1.9420	155.95	1.944	1.2333	0.032804	2.252	0.046627	1.1486

TABLE II.—SOLUBILITY OF CALCIUM SULFATE (*a*) IN SOLUTIONS OF POTASSIUM NITRATE.

G. salt added per liter of solution (KNO_3.)	d_4^{25} of added salt solution.	Equivalent concentration per liter of solution (KNO_3).	G. added salt per 1000 g. water.	G. added salt per 1000 g. solution	G. Ca SO_4 per 1000 g. solution.	G. Ca SO_4 per liter of solution.	Equivalent concentration per liter ($CaSO_4$).	G. Ca SO_4 per 1000 g. water.	Specific conductance of mixture.	d_4^{25} of mixture.
0	0	0	0	0	2.0854	2.0835	0.030604	2.0897	0.0022148	0.99911
2.786	0.99876	0.027554	2.797	2.7824	2.454	2.4571	0.036092	2.4669	0.0059355	1.0013
5.326	1.0004	0.052675	5.352	5.3106	2.7268	2.7347	0.040169	2.7489	0.0090808	1.0029
10.421	1.0036	0.10307	10.492	10.330	2.862	2.8870	0.42407	2.9002	0.014985	1.0088
				(*b*) in Solutions of Magnesium Sulfate.						
($MgSO_4$).		($MgSO_4$).								
0.0	...	0.0	0.0	0.0	..	....	....	....	....	....
0.6027	0.9977	0.10013	0.6044	0.60294	1.9565	1.9557	0.028726	1.9615	0.0026642	0.99960
1.2168	0.9983	0.020216	1.2190	1.2167	1.848	1.8482	0.027148	1.8537	0.003139	1.0001
1.8351	0.999	0.030488	1.8403	1.8339	1.777	1.7781	0.026119	1.7834	0.0036181	1.00067
				(*c*) Solubility of Selenite Plates in Solutions of Magnesium Sulfate.						
0	...	0	0	....	..	2.064	0.030317	2.0703	0.0022115	0.99905
0	...	0	0	....	..	2.055	0.030185	3.0613	0.0022115	0.99905
1.3376	...	0.022223	1.3413	....	..	1.7838	0.026201	1.7886	0.0034042	1.0004
3.3057	...	0.054921	3.3161	....	..	1.6417	0.024114	1.6469	0.0045499	1.0018
6.293	...	0.10455	6.3148	....	..	1.5538	0.022823	1.5592	0.0066165	1.0044
12.336	...	0.20495	12.385	....	..	1.4953	0.021964	1.5912	0.010415	1.0099

TABLE III.—EQUIVALENT CONDUCTANCE OF MAGNESIUM SULFATE AT 18° AND AT 25°.
(CONCENTRATIONS IN EQUIVALENTS PER LITER, CONDUCTANCE IN RECIPROCAL OHMS.)

Concentration.	$\Lambda_{18°}$.	Λ/Λ_o.	$\Lambda_{25°}$.	Λ/Λ_o.
0.00	135.0	100.00	114.4	100.00
0.00050635	123.3	91.33	104.7	91.52
0.0010147	117.4	86.96	100.1	87.50
0.0020094	110.8	82.08	94.67	82.75
0.005023	99.0	73.33	84.35	73.73
0.010047	88.85	65.82	76.15	66.56
0.020094	78.98	58.50	67.23	58.77
0.050235	66.05	48.93	56.54	49 37
0.10047	57.79	42.81	49.58	43.34
0.20094	49.82	36.90	43.12	37.69
0.50235	40.72	30.16	35.25	30.81
1.0067	33.37	24.72	28.81	25.18

TABLE IV.—CONDUCTANCE OF CALCIUM SULFATE SOLUTIONS. (*a*) AT 25°.

Equivalents per liter × 10^3.	Specific conductance × 10^5. 1/ohm.	Λ. 1/ohm.	Λ/Λ_o.	d_4^{25}.
0.0	..	140.0	100.00	..
0.099955	1.3657	136.63	97.59	..
0.19955	2.650	132.88	94.91	..
0.49795	6.343	127.38	90.98	..
0.9959	12.104	121.57	86.84	..
1.9975	22.612	13.20	80.86	0.99720
5.011	50.195	100.15	71.53	0.99748
10.081	90.17	89.45	63.89	0.99782
30.610	221.48	72.35	51.68	0.99911
36.408	252.0	69.21	49.44	(Hulett)
		(*b*) AT 18°.		d_4^{18}.
0.0	..	119.00	100.00	..
0.10013	1.1644	116.28	97.80	..
0.19986	2.2670	113.43	95.32	..
0.49871	5.436	109.0	91.60	..
0.99755	10.407	103.82	87.24	..
2.007	19.446	97.19	81.67	..
5.023	43.270	86.20	72.44	0.99895
10.096	77.96	77.21	64.88	0.99897

TABLE V.—CONDUCTANCE OF COPPER SULFATE SOLUTIONS AT 25°.

Equivalent concentration	Specific conductance × 10^3 1/ohm.	Λ. 1/ohm.	d_4^{25}.
0.025156	1.7286	86.50	0.99950
0.050202	2.9688	59.13	1.0013
0.100081	5.0609	50.56	1.0053
0.201085	8.7545	43.53	1.0136
0.41993	15.535	36.99	1.0307
1.9335	46.082	23.83	1.14645

Table VI.

Ionization of Salts in Mixtures Containing (*a*) Copper Sulfate or (*b*) Magnesium Sulfate in which Calcium Sulfate is the Saturating Salt, Calculated on the Assumption that Complex or Intermediate Ions are not Present. (Concentrations in Equivalents per Liter.)

Total concn. ($CuSO_4$).	Solubility. $CaSO_4$.	Solubility un-ionized. $CaSO_4$.	Concn. Ca^{++} ions.	Σi or concn. $SO_4^{=}$ ions.	Solubility product $Ca^{++} \times SO_4^{=} \times 10^4$.	Concn un-ionized ($CuSO_4$).	Concn. ions (Cu^{++}).	Specific conductance of mixture $\times 10^3$.	
								Calc.	Det.
0.0	0.030604	0.014788	0.015816	0.015816	2.503	0.0	0.0	2.2142	2 2148
0.025010	0.027113	0.014353	0.012760	0.02376	3.032	0.01401	0.0110	3.2393	3.1580
0.09992	0.024711	0.015121	0.009590	0.04587	4.398	0.06365	0.03628	6.1352	6.1348
0.20147	0.024767	0.016197	0.008570	0.07285	6.243	0.13719	0.6428	9.6912	9.6798
0.42358	0.026493	0.018503	0.007990	0.12280	9.811	0.30878	0.1148	16.284	16.383
1.9420	0.032804	....	....	....	...	...	...	...	46.627
($MgSO_4$.)						($MgSO_4$.)	Mg^{++}.		
0.0	0.030604	0.014788	0.015816	0.015816	2.503	...	0.0	2.214	2.11
0.010013	0.028726	0.014576	0.014150	0.01934	2.735	...	0.00519	2.681	2.664
0.020216	0.027148	0.014303	0.012845	0.02294	2.941	...	0.01005	3.155	3.139
0.030488	0.026119	0.014210	0.01191	0.02655	3.162	0.01585	0.01464	3.645	3.618
0.054921	0.024114	0.014084	0.01003	0.03500	3.510	0.03002	0.0247	...	...
0.10455	0.022823	0.01392	0.00890	0.05190	4.630	0.06155	0.0430	...	...
0.20495	0.021964	....	....	....	...	...	...	...	...

Table VII.

Ionization of Salts in Mixtures of Calcium Sulfate and Potassium Nitrate in which Calcium Sulfate is the Saturating Salt. (Concentrations in Equivalents Per Liter.)

Total concn. KNO_3.	Total solubility. $CaSO_4$.	Concn. $CaSO_4$ un-ionized.	Concn. Ca^{++} ions.	Concn. $SO_4^{=}$ ions.	Σi = total ion concentration.	Solubility product $Ca \times SO_4 \times 10^4$.	Concn. KNO_3 un-ionized.	C_{K^+}.	$C_{NO_3^-}$.	$C_{(CaNO_3)_2}$.	$C_{K_2SO_4}$.	Specific conductance $\times 10^3$.	
												Calc.	Det.
0.0	0.030604	0.014790	0.01582	0.01582	0.01582	2.503	0.0	0.0	0.0	0.0	0.0	2.2142	2.2115
0.027554	0.036092	0.013553	0.01955	0.01955	0.04195	3.821	0.001779	0.0224	0.0224	0.00302	0.00348	6.008	5.936
0.052675	0.040169	0.01322	0.02192	0.02192	0.06400	4.805	0.00508	0.04207	0.04207	0.00503	0.00550	9.158	9.081
0.1236	0.04820	0.013126	0.02600	0.02600	0.1210	6.760	0.01872	0.0950	0.0950	0.009148	0.00970	..	..

been shown, in previous papers of this series, to be connected with the formation of complex ions, double salts, or intermediate ions.

Another indication of the presence of intermediate or complex ions is that the solubility product as calculated from the solubility measurements increases more rapidly than when such ions are absent. This is because the calculations of the ionization count a part of the material present as intermediate, as being in the form of simple ions, and since the concentration of the intermediate ion increases rapidly with the concentration,

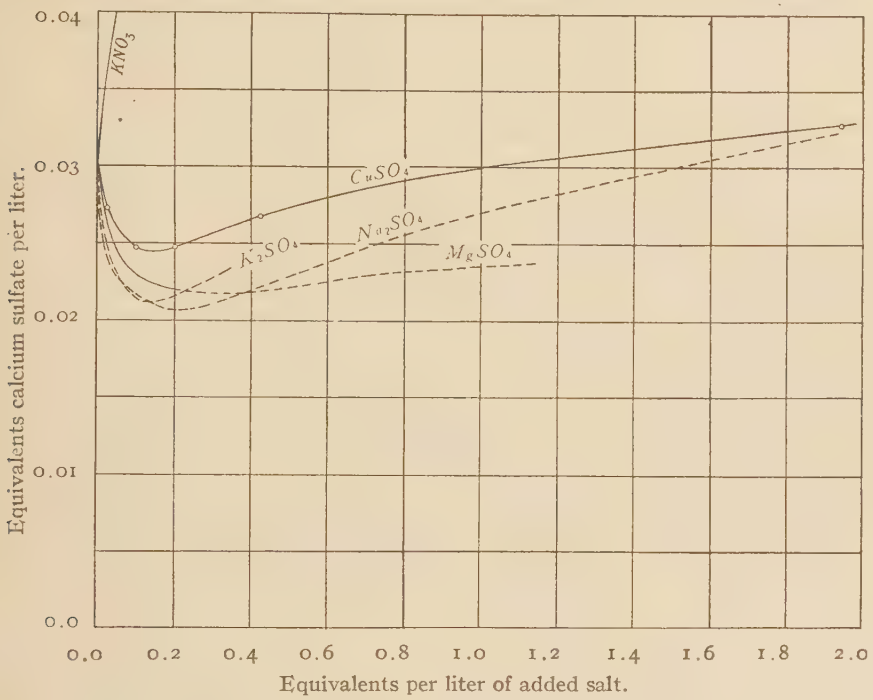


Fig. 1.—Solubility of calcium sulfate in solutions of other salts. Note that the solubility *decrease* when the concentration of the added salt is only 0.1 equivalents is very much less than corresponds to the solubility-product principle. At higher concentrations the curves take on the form of *non-common* ion curves.

this leads to an apparent rapid increase of the solubility product. It has been shown in a former paper that when account is taken of the intermediate ions in solutions of uni-bivalent salts, the solubility product as calculated becomes much more constant. Fig. 2 indicates that the solubility product of a bi-bivalent salt, calculated on the *usual assumption* that intermediate and complex ions are absent, increases with extreme rapidity as the concentration of the solution (the total ion concentration) increases. Thus, when copper sulfate is the added salt, the solu-

bility product is increased to more than 3 times its smallest value before the total ion concentration has reached 0.1 *N*, so the apparent activity of the bivalent ions *decreases very rapidly* with increasing ion concentration. It is, of course, possible that the *whole* of such a very rapid increase

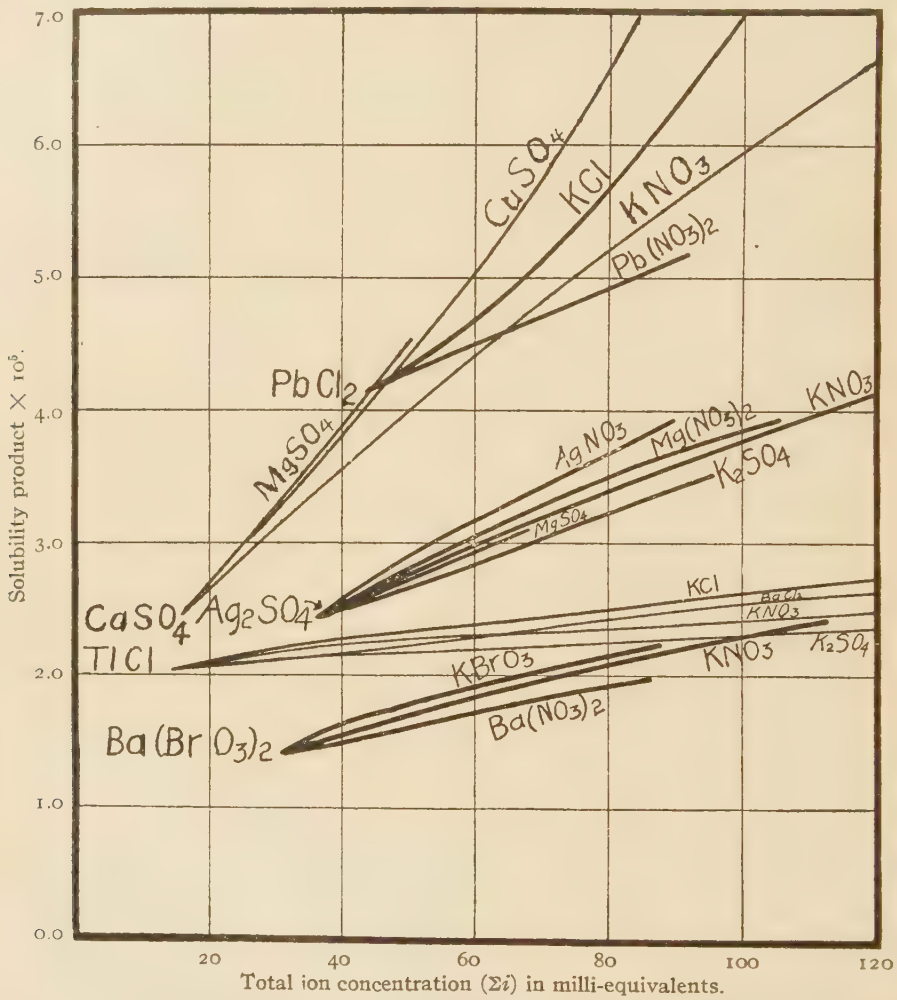
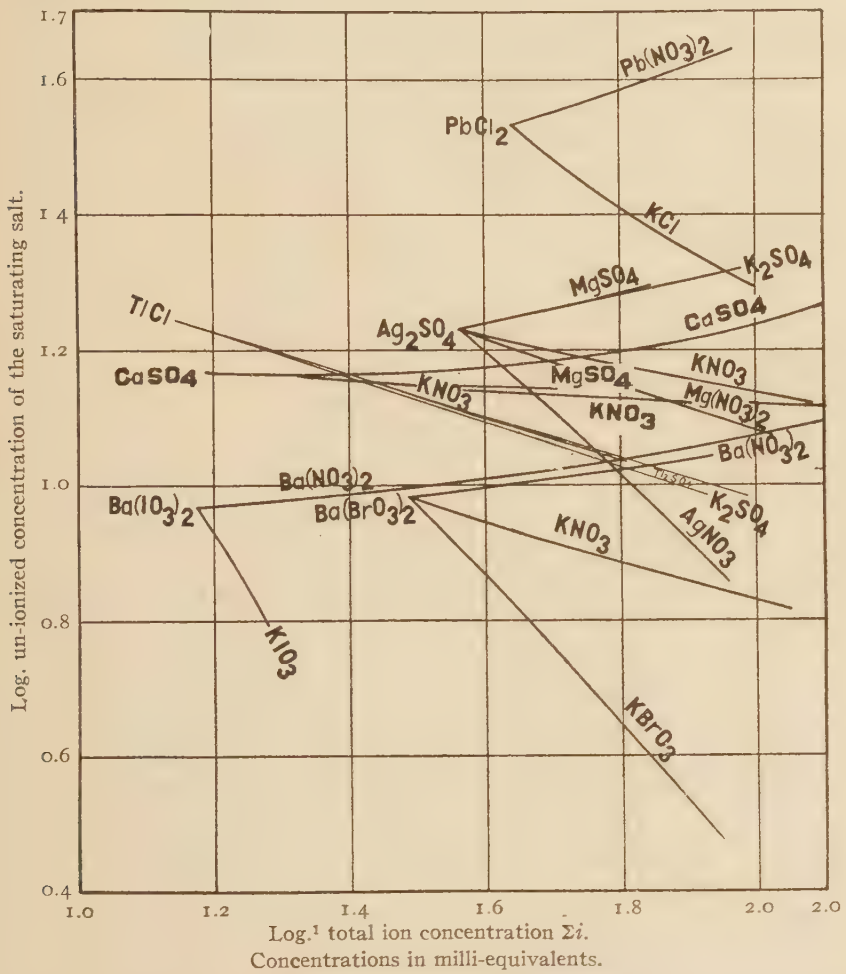


Fig. 2.—The solubility product for uni-univalent, uni-bivalent, and bi-bivalent salts, calculated on the assumption that intermediate ions are absent.

in the solubility product of salts of this class, cannot be explained by the assumption of the existence of complex ions.

The solubility of the un-ionized part of the salt as calculated on the assumption that intermediate ions and other complexes are absent (Fig. 3) is much more constant than it was found to be for uni-uni- and uni-bi-

valent salts, except in the more concentrated solutions in which copper sulfate is the added salt. The change in the slope of these curves as compared with those for the uni-univalent salts, is in the same direction as that for uni-bivalent salts when the common bivalent ion is added, that is the change in slope is in the direction to be expected if intermediate ions are present.



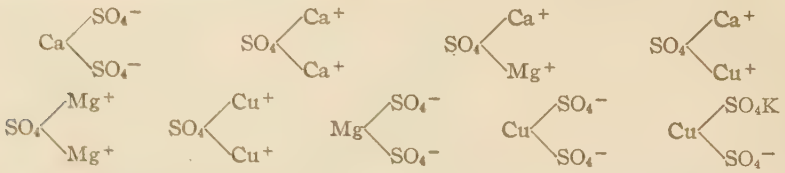
Log.[1] total ion concentration Σi.
Concentrations in milli-equivalents.

Fig. 3.—The concentration of the un-ionized part of uni-univalent (TlCl), uni-bivalent ($Ba(IO_3)_2$, $Ba(BrO_3)_2$, Ag_2SO_4, $PbCl_2$) and bi-bivalent ($CaSO_4$) salts in their saturated solutions in the presence of other salts, calculated on the incorrect consumption that intermediate ions are absent.

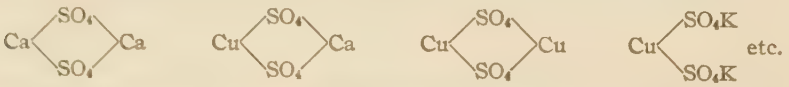
[1] The curves for *barium iodate* should be *ten squares lower down* and *five squares further to the left.* Note how closely these curves parallel those for barium bromate in spite of their large displacement.

It is to be *specially noted that most of the results described above were obtained in dilute solutions,* that is below 0.1 N total ion concentration, and that therefore they are not to be considered from the standpoint of much of the work in the literature in regard to the formation of double or complex salts in concentrated solutions. The formation of these latter double and complex salts is highly specific, while that for which evidence is obtained in this paper will undoubtedly be found to be general, just as the similar behavior of uni-bivalent salts described in the first paper of this series, was later proved to be perfectly general.

As has been suggested in the first part of this paper, a large part of this abnormal behavior of bi-bivalent salts would be only apparent if complex bivalent ions are formed. These would have the form



and would form salts of a ring structure:



Since the formation of such intermediate ions or ring or double salts stores the materials in forms in which they do not enter into the primary equilibrium between the solid, the un-ionized part of the salt consisting of single molecules, and the ordinary ions,[1] it increases what is called the solubility of the salt by approximately the amount of the material put into such forms. This is similar to the increase in the solubility of a salt by metathesis. The complex ions do not enter into the simple solubility product equilibrium, as it actually is, but since they carry the current, they make the apparent number of simple ions greater than accords with the facts, so that the solubility product calculated on the basis of the apparent number instead of the real number of simple ions, comes out too large, and since the number of intermediate ions increases rapidly with the concentration, the apparent solubility product, also increases very rapidly.

The equivalent solubility S_o of a salt which dissociates in the above manner may be given as follows:

$$S_o = 2(AB)_o + 4(A_2B_2)_o + 2(B_o) + 2(ABA)_o + 4(BAB)_o,$$

where AB represents the number of mols of the un-ionized single mole-

[1] When this series of researches was begun in 1910 it was the intention to investigate complex formation in salts of the uni-univalent type. Since that time this problem has been taken up by G. McP. Smith and his students in a series of comprehensive studies. See *J. Am. Chem. Soc.*, **40**, 1802 (1918).

cules, A_2B_2 of the double molecules, B of the positive ion, ABA of the negative intermediate ion, and BAB of the positive intermediate ion. A more complete analysis for the similar case of a uni-bivalent salt has already been given in a former paper of this series.[1]

In solutions of uni-bivalent salts, in addition to intermediate ions such as KSO_4^-, ions of the type of $K\text{–}SO_4\text{–}SO_4^-$ are to be expected, while in concentrated solutions of uni-univalent salts, there is much probability that double molecules such as K_2Cl_2, and their complex or intermediate ions, K_2Cl^+ and KCl_2^- exist.[1]

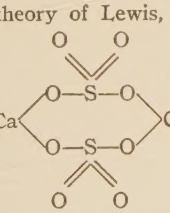
While the evidence for the existence of complex ions in solutions of bi-bivalent salts is neither so complete or so perfect as that obtained in solutions of uni-bivalent salts from the standpoint of the solubility results obtained thus far, there is an independent line of evidence which could not be obtained in the latter case; that is the mobility of the ions in bi-bivalent salt solutions decreases rapidly as the concentration of the solution increases. This change is in the direction to be expected if complex ions are present. Such complex ions differ from the complex ions usually considered in the literature in that the evidence points to their existence in dilute solutions, just as is the case with intermediate ions. In this respect the complex ions considered in this paper are more like such intermediate ions; and so might well be called intermediate ions, since they are intermediate between the single and the double molecules of the salt.

Summary.

1. It has been shown in former papers by Harkins and his co-workers that salts of the tri-ionic and still higher types ionize in steps and give, even in 0.1 or 0.1 N solutions, a very considerable percentage of intermediate ions. The present paper shows that the solubility relations of calcium sulfate when common ions are added, are very similar to those of such higher type salts. This indicates the probability that complex ions, such as $Ca(SO_4)_2^{--}$ and $Ca_2SO_4^{++}$ are present in the solutions. These complex ions differ from what are usually considered under this designation, since they are present to a considerable extent in dilute solutions, so in this sense they are more like intermediate ions.

2. If it is assumed that such complex ions are absent, the solubility prod-

[1] According to the octet theory of Lewis, lately amplified by Langmuir, these salts would have the structure



where each bond represents a pair of electrons, common to two octets.

uct calculated on this basis is found to increase with great rapidity as the concentration increases; thus, if the total ion concentration increases from 0.02 to 0.10 *N* the solubility product is tripled, so, if only simple ions are present their activity decreases very rapidly with an increase in concentration. On the other hand, the solubility found for the un-ionized part on the basis of this assumption, remains much more constant than in the case of uni-univalent salts. The change in the slope of these curves is in the direction which is to be expected if complex ions are present.

3. The percentage concentration of such complexes is much higher in copper sulfate than in magnesium sulfate solutions, at the lower concentrations.